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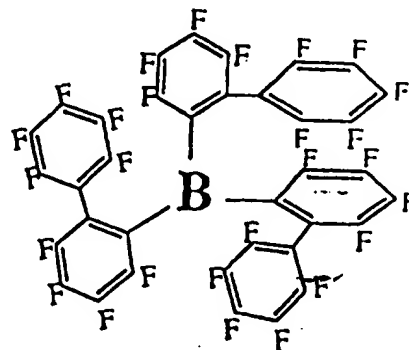
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**(54) Title:** AN ORGANO-LEWIS ACID AS COCATALYST FOR CATIONIC HOMOGENEOUS METALLOCENE ZIEGLER-NATTA OLEFIN POLYMERIZATIONS

**(57) Abstract**

The synthesis of the organo-Lewis acid perfluorobiphenylborane (PBB) and the activation of metallocenes for the formation of a variety of highly active homogeneous Ziegler-Natta metallocene olefin polymerization, copolymerization and ring-opening polymerization catalysts is described.



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**AN ORGANO-LEWIS ACID AS COCATALYST FOR CATIONIC  
HOMOGENEOUS METALLOCENE ZIEGLER-  
NATTA OLEFIN POLYMERIZATIONS**

This invention was made with Government support under Contract No. DE-FG02-86ER13511 awarded by the Department of Energy. The Government has certain rights in this invention.

5     **Background of the Invention**

This invention relates to the compositions of matter useful as catalysts, to a method for preparing these catalysts and to a method for polymerization utilizing the catalysts.

10     The use of soluble Ziegler-Natta type catalysts in the polymerization of olefins is well known in the prior art. In general, such systems include a Group IV-B metal compound and a metal or metalloid alkyl cocatalyst, such as aluminum alkyl cocatalyst. More broadly, it may be said to include a mixture of a Group I-III metal alkyl and a transition metal complex from Group IVB-VB metals, particularly titanium, zirconium, or hafnium with aluminum alkyl cocatalysts.

15     First generation cocatalyst systems for homogeneous metallocene Ziegler-Natta olefin polymerization, alkylaluminum chlorides ( $\text{AlR}_2\text{Cl}$ ), exhibit low ethylene polymerization activity levels and no propylene polymerization activity. Second generation cocatalyst systems, utilizing methyl aluminoxane (MAO), raise activities by several orders of magnitude. In practice however, a large stoichiometric excess of MAO over catalyst ranging  
20     from several hundred to ten thousand must be employed to have good activities and stereoselectivities. Moreover, it has not been possible to isolate characterizable metallocene active species using MAO. The third generation of cocatalyst,  $\text{B}(\text{C}_6\text{F}_5)_3$ , proves to be far more efficient while utilizing a 1:1 catalyst-cocatalyst ratio. Although active catalyst species generated with  $\text{B}(\text{C}_6\text{F}_5)_3$  are isolable and characterizable, the anion  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  formed after  
25      $\text{Me}^-$  abstraction from metallocene dimethyl complexes is weakly coordinated to the electron-deficient metal center, thus resulting in a drop of certain catalytic activities. The recently developed  $\text{B}(\text{C}_6\text{F}_5)_4^-$  type of non-coordinating anion exhibits some of the highest reported catalytic activities, but such catalysts have proven difficult to obtain in the pure state due to poor thermal stability and poor crystallizability, which is crucial for long-lived catalysts and  
30     for understanding the role of true catalytic species in the catalysis for the future catalyst

design. Synthetically, it also takes two more steps to prepare such an anion than for the neutral organo-Lewis acid.

### Summary of the Invention

Accordingly, it is an object of the subject invention to prepare and utilize a new class of olefin polymerization catalysts.

A further object of the subject invention is a catalyst which permits better control over molecular weight, molecular distribution, stereoselectivity, and comonomer incorporation.

Another object of the subject invention is a Ziegler-Natta type catalyst system which reduces the use of excess cocatalyst and activates previously unresponsive metallocenes.

These and other objects are attained by the subject invention whereby in one embodiment, a strong organo-Lewis acid, such as perfluorobiphenylborane (PBB) is utilized as a highly efficient cocatalyst for metallocene-mediated olefin polymerization and as a catalyst for a ring opening polymerization of THF. PBB can be synthesized in much higher yield than  $B(C_6F_5)_3$  and the anion generated with PBB is non-coordinating instead of weakly coordinating as in the case of  $B(C_6F_5)_3$ . Thus, the former exhibits higher catalytic activities and can activate previously unresponsive metallocenes. The catalytically active species generated with PBB are isolable, X-ray crystallographically characterizable instead of the unstable, oily residues often resulting in the case of  $B(C_6F_5)_4^-$ . In addition, PBB exhibits even higher catalytic activities in most cases.

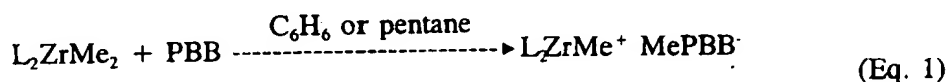
In one embodiment of the subject invention a strong organo-Lewis acid, such as perfluorobiphenylborane (PBB), is utilized to synthesize stoichiometrically precise, isolable/crystallographically characterizable, highly active "cation-like" metallocene polymerization catalysts. The biphenyl groups of PBB may be connected to the Boron at the meta, para, or ortho position.

PBB reacts with early transition metal or actinide alkyls to yield highly reactive cationic complexes:  $(LL'MR)^+(RBR'R''_2)^-$ .

where  $L, L' = C_5H_nR_{5-n}$ , indenyl, allyl, benzyl,  $C_5H_nR_{4-n}XNR$   
 $M =$  early transition metal or actinide, *e.g.*, Ti, Zr, Hf, Th, U;  
 $X = R_2'''Si, R'''$  bridging alkyl or aryl group ( $C \leq 10$ )

- R, R''' = alkyl, benzyl, or aryl group ( $C \leq 20$ ), hydride, silyl;  
 B = Boron  
 R' = fluorinated biphenyl  
 R'' = fluorinated phenyl, fluorinated biphenyl, or fluorinated polycyclic fused rings such as naphthyl, anthryl, or fluorenyl

5 As a specific example of the above, the reaction of PBB with a variety of zirconocene dimethyl complexes proceeds rapidly and quantitatively to yield, after recrystallization from hydrocarbon solvents, the catalytic complex of Eq. 1.



10 Such catalytic complexes have been found to be active homogeneous catalysts for  $\alpha$ -olefin polymerization and, more particularly, the polymerization, copolymerization or oligopolymerization of ethylene,  $\alpha$ -olefins, dienes and acetylenic monomers, as well as intramolecular C-H activation.

15 The cocatalyst of the subject invention may be referred to as BR'R'', where B = Boron; R' and R'' represent at least one and maybe more fluorinated biphenyls or other polycyclic groups, such as naphthyl. Two of the biphenyls may be substituted with a phenyl group. Both the biphenyls and the phenyl groups should be highly fluorinated, preferably with only one or two hydrogens on a group, and most preferably, as in PBB with no  
 20 hydrogens and all fluorines.

The cocatalyst system of the subject invention can be better understood with reference to the drawings wherein:

Fig. 1 is a structural depiction of PBB;

Fig. 2 is a reaction pathway for the synthesis of PBB;

25 Fig. 3 shows the reaction pathway for a catalyst system according to the subject invention;

Fig. 4 shows the reaction pathway for a second catalyst system according to the subject invention;

Fig. 5 shows the reaction pathway for a third catalyst system according to the subject invention; and

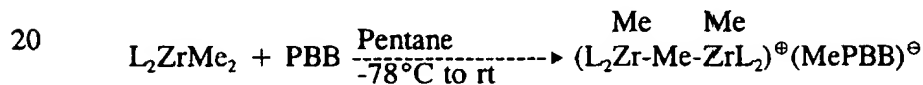
30 Fig. 6 shows the reaction pathway for a fourth catalyst system according to the

subject invention.

### Detailed Description of the Invention

5           The reaction of perfluorobiphenylborane with a variety of zirconocene and other actinide or transition metal dimethyl complexes proceeds rapidly and quantitatively at room temperature in noncoordinating solvents to yield, after recrystallization, complexes. This catalytic reaction may be used in the polymerization, copolymerization, oligomerization and dimerization of  $\alpha$ -olefins. In addition, the catalyst of the subject invention may be used as  
10           a cocatalyst in conjunction with aluminum alkyls, aluminum aryls, ( $\text{AlR}_3$ ,  $\text{R} = \text{Et}$ ,  $\text{Me}$ ,  $\text{Ph}$ , naphthyl) or methyl alumoxane ( $\text{Al}(\text{CH}_3)_2\text{O}$ ) $_n$  for increased polymer yields.

          PBB (FIG. 1) has been synthesized in quantitative yields of 91% as compared to the 30-50% yields experienced with  $\text{B}(\text{C}_6\text{F}_5)_3$ , currently a very important Lewis acidic cocatalyst in industry (FIG. 2). The Lewis acidity of PBB has been shown to be much  
15           greater than that of  $\text{B}(\text{C}_6\text{F}_5)_3$  by comparative reactions of  $\text{Cp}'_2\text{ThMe}_2$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  and PBB ( $\text{Cp}' = \text{C}_5\text{Me}_5$ ). The former reagent does not effect  $\text{Me}^-$  abstraction, while the latter gives the catalyst shown in FIG. 3. The reaction of PBB with a bis-Cp type of dimethyl zirconocenes forms a dinuclear methyl-bridged zirconocene cation such as



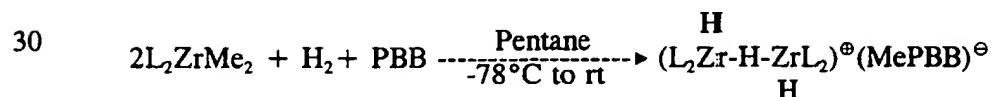
(1:1 or 2:1)

where  $\text{L} = \text{C}_5\text{H}_5$

25            $\text{L} = \text{C}_5\text{H}_3\text{Me}_2$  or

$\text{L} = \text{C}_5\text{Me}_5$

and a hydride-bridged analog such as

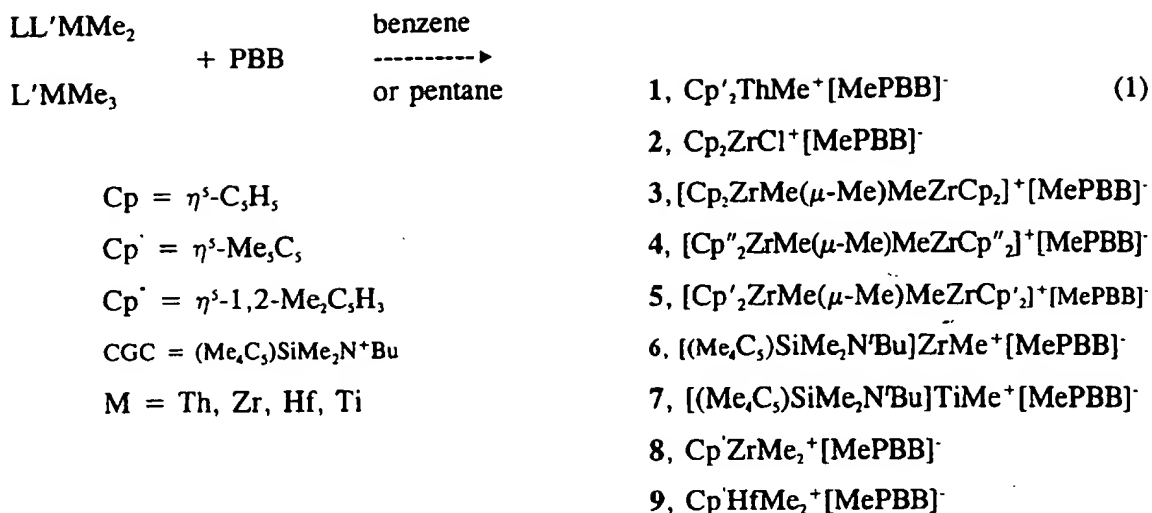


where  $\text{L} = \text{C}_5\text{H}_5$  or

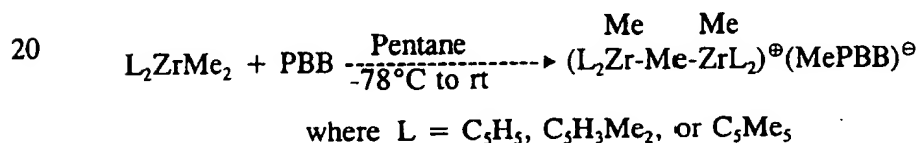
35            $\text{L} = \text{C}_5\text{H}_3\text{Me}_2$

More particularly, reaction of PBB with group 4 and Th methyls proceeds cleanly to yield cationic complexes such as set forth below.





For ethylene polymerization, catalytic activities of dinuclear cations generated from PBB are greater than those of monomeric cations generated from  $\text{B}(\text{C}_6\text{F}_5)_3$  presumably because  $(\text{MePBB})^-$  is a non-coordinating anion as compared to the weakly coordinating anion  $\text{MeB}(\text{C}_6\text{F}_5)_3$ . The dinuclear cations have also been found to catalyze the rapid ring-opening polymerization of THF to produce poly(tetrahydrofuran), an important thermoplastic elastomer and artificial leather. Monomeric zirconocene cations have also been generated *in situ* by the reaction of  $\text{L}_2\text{ZrMe}_2$  and PBB at  $60^\circ\text{C}$



OR



These attempts show very high activities for olefin polymerization, and identify  $(\text{MePBB})^-$  to be a truly non-coordinating anion. The polymerization data with metallocene cations having various anions are summarized in Table 1.

Table 1. Polymerization Data

| entry no. | catalyst   | $\mu\text{mol}$ of cat | conditions                   | monomer(s) <sup>a</sup> | polymer yield (g) | activity <sup>b</sup> | $M_{wd}^c$ ( $10^{-3}$ ) | $M_w/M_n$ remarks           |
|-----------|--|------------------------|------------------------------|-------------------------|-------------------|-----------------------|--------------------------|-----------------------------|
| 1.        | $(\text{Cp}_2\text{ZrMe})_2\text{Me}^+$<br>MePBB <sup>-</sup>          | 15                     | 100 mL toluene<br>25°C, 40 s | ethylene                | .80               | $4.80 \times 10^6$    | 559                      | 3.06                        |
| 2.        | $\text{Cp}_2\text{ZrMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_3^-$   | 15                     | 100 mL toluene<br>25°C, 60 s | ethylene                | 1.00              | $4.00 \times 10^6$    | 124                      | 2.03                        |
| 3.        | $(\text{Cp}''_2\text{ZrMe})_2\text{Me}^+$<br>MePBB <sup>-</sup>        | 15                     | 100 mL toluene<br>25°C, 40 s | ethylene                | 1.30              | $7.80 \times 10^6$    | 392                      | 2.72                        |
| 4.        | $\text{Cp}''_2\text{ZrMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_3^-$ | 15                     | 100 mL toluene<br>25°C, 60 s | ethylene                | 1.50              | $6.00 \times 10^6$    | 321                      | 1.42                        |
| 5.        | $(\text{Cp}'_2\text{ZrMe})_2\text{Me}^+$<br>MePBB <sup>-</sup>         | 15                     | 100 mL toluene<br>25°C, 60 s | ethylene                | 1.07              | $4.30 \times 10^6$    | 370                      | 2.28                        |
| 6.        | $\text{Cp}'_2\text{ZrMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_3^-$  | 15                     | 100 mL toluene<br>25°C, 60 s | ethylene                | 0.80              | $3.20 \times 10^6$    | 136                      | 2.54                        |
| 7.        | $\text{Cp}'\text{TiMe}_2^+$<br>MePBB <sup>-</sup>                      | 50                     | 5 mL toluene<br>25°C, 15 min | styrene                 | 0.35              | $1.61 \times 10^6$    | 170                      | 2.56 $[\text{rrrr}] > 98\%$ |
| 8.        | $\text{Cp}'\text{ZrMe}_2^+$<br>MePBB <sup>-</sup>                      | 50                     | 5 mL toluene<br>25°C, 10 min | styrene                 | 1.45              | $1.00 \times 10^7$    | 27.6                     | 2.63 atactic                |
| 9.        | $\text{Cp}'\text{HfMe}_2^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_3^-$  | 50                     | 5 mL toluene<br>25°C, 15 min | styrene                 | 0.69              | $3.17 \times 10^6$    | 24.8                     | 2.98 atactic                |
| 10.       | $\text{Cp}'\text{HfMe}_2^+$<br>MePBB <sup>-</sup>                      | 50                     | 5 mL toluene<br>25°C, 15 min | styrene                 | 1.16              | $5.33 \times 10^6$    | 22.9                     | 2.78 atactic                |

|     |  |    |                                |                      |      |                    |      |      |                               |
|-----|--|----|--------------------------------|----------------------|------|--------------------|------|------|-------------------------------|
| 11. | $\text{Cp}^*\text{TiMe}_2$<br>$\text{MeB}(\text{C}_6\text{F}_5)_2$ | 50 | 25 mL toluene<br>25°C, 5 min   | ethylene<br>1-hexene | 0.70 | $1.70 \times 10^3$ | 848  | 23.7 | 39.5% hexene<br>incorporation |
| 12. | $\text{Cp}^*\text{TiMe}_2$<br>$\text{MePBB}^+$                     | 50 | 25 mL toluene<br>25°C, 5 min   | ethylene<br>1-hexene | 4.51 | $1.08 \times 10^6$ | 151  | 4.32 | 43.6% hexene<br>incorporation |
| 13. | $\text{CGCZrMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_2$         | 15 | 100 mL toluene<br>25°C, 20 min | ethylene             | 0    |                    |      |      |                               |
| 14. | $\text{CGCZrMe}^+$<br>$\text{MePBB}^+$                             | 15 | 100 mL toluene<br>25°C, 4 min  | ethylene             | 1.56 | $1.56 \times 10^6$ | 7.69 | 2.78 |                               |
| 15. | $\text{CGCTiMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_2$         | 15 | 100 mL toluene<br>25°C, 10 min | ethylene             | 0.21 | $8.40 \times 10^4$ | 1058 | 9.54 |                               |
| 16. | $\text{CGCTiMe}^+$<br>$\text{MePBB}^+$                             | 15 | 100 mL toluene<br>25°C, 40 s   | ethylene             | 0.83 | $4.98 \times 10^6$ | 305  | 2.56 |                               |
| 17. | $\text{CGCZrMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_2$         | 50 | 25 mL toluene<br>25°C, 15 min  | ethylene<br>1-hexene | 0    |                    |      |      |                               |
| 18. | $\text{CGCZrMe}^+$<br>$\text{MePBB}^+$                             | 50 | 25 mL toluene<br>25°C, 15 min  | ethylene<br>1-hexene | 6.97 | $5.58 \times 10^3$ | 10.0 | 2.68 | 33.6% hexene<br>incorporation |
| 19. | $\text{CGCTiMe}^+$<br>$\text{MeB}(\text{C}_6\text{F}_5)_2$         | 25 | 25 mL toluene<br>25°C, 10 min  | ethylene<br>1-hexene | 0.05 | $1.20 \times 10^4$ |      |      | 63.2% hexene<br>incorporation |
| 20. | $\text{CGCTiMe}^+$<br>$\text{MePBB}^+$                             | 25 | 25 mL toluene<br>25°C, 10 min  | ethylene<br>1-hexene | 1.95 | $4.68 \times 10^3$ | 105  | 1.86 | 65.3% hexene<br>incorporation |

<sup>a</sup> 1 atm ethylene pressure; 17.4 mmol of styrene, and 44.5 mmol of 1-hexene. <sup>b</sup> g polymer/[(mol of cationic metallocene)atm·h], except in entries 7-10: polystyrene/[(mol catalyst)(mol monomer)h] (reproducibility between runs  $\approx 10 \sim 15\%$ ). <sup>c</sup> GPC relative to polystyrene standards.

Other types of cationic metallocene catalyst systems can also be created with PBB. Metallocene cations of mono-Cp type (FIGs. 4 and 5) have been formed by the reaction of mono-pentamethyl Cp trimethyl group IV complexes with and PBB. These are very good syndiospecific styrene polymerization catalysts (FIGs. 4 and 5). Constrained geometry types of zirconocene and titanocene cations such as those in FIG. 6 where  $m = \text{Zr, Ti}$ , are readily produced by the reaction of the corresponding dimethyl metallocenes with PBB. They are highly naked cations and much more active catalysts than those generated with  $\text{B}(\text{C}_6\text{F}_5)_3$ .

## EXAMPLES

### EXAMPLE 1

#### Synthesis of perfluorobiphenylborane (PBB)

*n*-Butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) was added dropwise to bromopentafluorobenzene 18.0 g, 9.1 mL, 72.9 mmol) in 100 mL of diethyl ether over a cold-water bath. The mixture was then stirred for a further 12 h at room temperature. Removal of solvent followed by vacuum sublimation at  $60\text{--}65^\circ\text{C}/10^{-4}$  torr gave 12.0 g of 2-bromononafluorobiphenyl as a whiter crystalline solid: yield 83.3%. The dangerous and explosive nature of  $\text{C}_6\text{F}_5\text{Li}$  ether solutions in this preparation can be avoided by (a) the use of excess of  $\text{C}_6\text{F}_5\text{Br}$ , (b) slow addition of *n*-butyllithium, (c) frequent change of the cold water bath or use of a continuous flowing cold water bath.

To the above prepared 2-bromononafluorobiphenyl (5.0 g, 12.7 mmol) in a mixed solvent of 70 mL of diethyl ether and 70 mL of pentane was gradually added 8.0 mL of *n*-Butyllithium (1.6 M in hexanes, 12.8 mmol) at  $-78^\circ\text{C}$ . The mixture was stirred for an additional 2 h, and boron trichloride (4.0 mL, 1.0 M in hexanes, 4.0 mmol) was then quickly added by a syringe. The mixture was left at  $-78^\circ\text{C}$  for 1 h and the temperature was then allowed to slowly rise to room temperature. A suspension resulted after stirring an additional 12 h. It was filtered to give a yellow solution, and the solvent of the filtrate was removed in vacuo. The resulting pale yellow powder was sublimed at  $140^\circ\text{C}/10^{-4}$  torr or  $125^\circ\text{C}/10^{-6}$  torr to produce a light yellow crystalline solid as an ether-free crude product. Recrystallization from pentane at  $-20^\circ\text{C}$  gave 3.5 g of the pure PBB as a white crystalline solid: yield 91.0%. Analytical and spectroscopic data for PBB are as follows.  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ):  $\delta$  -120.08 (s, br, 3 F, F-3), -132.09 (s, br, 3 F, F-6), -137.66 (s, br, 6 F, F-

2'/F-6'), -143.31 (t,  $^3J_{F-F} = 21.4$  Hz, 3 F, F-4), -149.19 (t,  $^3J_{F-F} = 21.7$  Hz, 3 F, F-4'), -150.56 (t,  $^3J_{F-F} = 14.7$  Hz, 3 F, F-5), -160.72 (s, br, 6 F, F-3'/F-5').  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  150.92 (dd,  $^1J_{C-F} = 251.8$  Hz,  $^2J_{C-F} = 10.1$  Hz, 3 C), 146.35 (dd,  $^1J_{C-F} = 254.3$  Hz,  $^2J_{C-F} = 12.1$  Hz, 3 C), 144.26 (dd,  $^1J_{C-F} = 258.1$  Hz,  $^2J_{C-F} = 10.5$  Hz, 6 C), 143.50 (tt,  $^1J_{C-F} = 265.4$  Hz,  $^2J_{C-F} = 12.0$  Hz, 3 C), 141.98 (tt,  $^1J_{C-F} = 261.4$  Hz,  $^2J_{C-F} = 11.7$  Hz, 3 C), 141.17 (tt,  $^1J_{C-F} = 254.3$  Hz,  $^2J_{C-F} = 10.5$  Hz, 3 C), 137.70 (tt,  $^1J_{C-F} = 257.3$  Hz,  $^2J_{C-F} = 11.6$  Hz, 6 C), 124.51 (d,  $^2J_{C-F} = 11.7$  Hz, 3 C), 113.60 (d,  $^2J_{C-F} = -11.5$  Hz, 3 C), 106.05 (s, br, 3 C). MS: parent ion at m/e 956. Anal. Calcd for  $\text{C}_{36}\text{BF}_{27}$ : C, 45.22; H, 0.00. Found: C, 45.44; H, 0.05.

## EXAMPLE 2

### Synthesis of $\text{Cp}'_2\text{ThMe}^+$ (MePBB) $^-$

$\text{Cp}'_2\text{ThMe}_2$  (0.106 g, 0.199 mmol) and PBB (0.191 g, 0.199 mmol) were in the glove box charged into a 25-mL reaction flask with a filter plug, and the flask was attached to the high vacuum line. Benzene (15 mL) was then vacuum-transferred into this flask at -78°C. The mixture was slowly allowed to warm to room temperature and stirred for 6 h. The solvent was removed, pentane (20 mL) was next vacuum-transferred into the flask, and the mixture was filtered after stirring. The white solid which collected was dried under vacuum to give 0.210 g of product: yield 70.9%. Analytical and spectroscopic data are as follows.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  1.61 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 0.62 (s, 3 H, Th-CH<sub>3</sub>), -095 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  -124.57 (s, br, 3F), -138.10 (s, br, 3 F), -139.28 (d,  $^3J_{F-F} = 21.4$  Hz, 3 F), -139.74 (d,  $^3J_{F-F} = 21.2$  Hz, 3 F), -155.08 (t,  $^3J_{F-F} = 21.4$  Hz, 3 F), -157.32 (t,  $^3J_{F-F} = 22.0$  Hz, 3 F), -162.20 (t,  $^3J_{F-F} = 22.0$  Hz, 3 F), -163.13 (t,  $^3J_{F-F} = 22.0$  Hz, 3 F), -163.90 (t,  $^3J_{F-F} = 21.4$  Hz, 3 F).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  129.54 ( $\text{C}_5\text{Me}_5$ ), 79.28 (Th-Me), 10.44 ( $\text{C}_5\text{Me}_5$ ), 10.25 (B-Me). Anal. Calcd for  $\text{C}_{58}\text{H}_{36}\text{BF}_{27}\text{Th}$ : C, 46.79; H, 2.44; N, 0.00. Found: C, 46.68; H, 2.24; N, 0.00.

## EXAMPLE 3

### Synthesis of $\text{L}_2\text{Zr}(\text{Me})(\mu\text{-Me})(\text{Me})\text{ZrL}_2^+$ (MePBB) $^-$ (L = $\text{C}_5\text{H}_5$ (Cp), $\text{C}_5\text{H}_3\text{Me}_2$ (Cp''), or $\text{C}_5\text{Me}_5$ (Cp'))

$\text{L}_2\text{ZrMe}_2$  (0.398 mmol) and PBB (0.199 mmol) were loaded into a 25 mL flask, which was then attached to the vacuum line. Pentane (20 mL) was then vacuum-

transferred into this flask at  $-78^{\circ}\text{C}$ . The mixture was slowly warmed to room temperature and stirred for an additional 2 h ( $\text{L} = \text{Cp}$ ), 15 h ( $\text{L} = \text{Cp}''$ ) or 48 h ( $\text{L} = \text{Cp}'$ ). The resulting suspension was filtered, and the colored solids (light pink for  $\text{Cp}$ , light yellow for  $\text{Cp}''$  and yellow for  $\text{Cp}'$ ) were washed with a small amount of pentane and dried under vacuum: yields 90.3% ( $\text{Cp}$ ), 86.3% ( $\text{Cp}''$ ) and 34.7% ( $\text{Cp}'$ ). Analytical and spectroscopic data for  $\text{L} = \text{C}_5\text{H}_5$  are as follows.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  5.65 (s, 20 H,  $\text{C}_5\text{H}_5$ ), -0.04 (s, 6 H,  $\text{Zr-CH}_3$ ), -0.84 (s, br, 3 H,  $\text{B-CH}_3$ ), -1.15 (s, 3 H,  $\text{Zr-CH}_3\text{-Zr}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  -124.20 (d,  $^3J_{\text{F-F}} = 16.6$  Hz, 3 F), -138.98 (d,  $^3J_{\text{F-F}} = 20.3$  Hz, 3 F), -139.20 (d,  $^3J_{\text{F-F}} = 22.0$  Hz, 3 F), -140.29 (d,  $^3J_{\text{F-F}} = 24.5$  Hz, 3 F), -155.15 (t,  $^3J_{\text{F-F}} = 20.9$  Hz, 3 F), -160.06 (t,  $^3J_{\text{F-F}} = 22.3$  Hz, 3 F), -162.79 (t,  $^3J_{\text{F-F}} = 22.0$  Hz, 3 F), -163.11 (t,  $^3J_{\text{F-F}} = 21.5$  Hz, 3 F), -163.97 (t,  $^3J_{\text{F-F}} = 19.0$  Hz, 3 F).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  113.24 ( $\text{C}_5\text{H}_5$ ), 38.88 ( $\text{Zr-CH}_3$ ), 21.53 ( $\text{B-CH}_3$ ), 15.80 ( $\text{Zr-CH}_3\text{-Zr}$ ). Anal. Calcd for  $\text{C}_{60}\text{H}_{32}\text{BF}_{27}\text{Zr}_2$ : C, 49.39; H, 2.21; N, 0.00. Found: C, 48.97; H, 1.92; N, 0.00.

Analytical and spectroscopic data for  $\text{L} = \text{C}_5\text{H}_3\text{Me}_2$  are as follows.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ,  $23^{\circ}\text{C}$ ):  $\delta$  5.51 (t,  $^3J_{\text{H-H}} = 2.8$  Hz, 4 H,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 5.47 (t,  $^3J_{\text{H-H}} = 3.2$  Hz, 4 H,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 5.18 (t,  $^3J_{\text{H-H}} = 2.8$  Hz, 4 H,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 1.73 (s, 12 H,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 1.51 (s, 12 H,  $\text{C}_5\text{H}_3\text{Me}_2$ ), -0.26 (s, 6 H,  $\text{Zr-CH}_3$ ), -0.92 (s, br, 3 H,  $\text{B-CH}_3$ ), -1.50 (s, 3 H,  $\text{Zr-CH}_3\text{-Zr}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  -123.37 (d,  $^3J_{\text{F-F}} = 15.3$  Hz, 3 F), -139.20 (d,  $^3J_{\text{F-F}} = 24.0$  Hz, 3 F), -139.62 (d,  $^3J_{\text{F-F}} = 24.3$  Hz, 3 F), -139.89 (d,  $^3J_{\text{F-F}} = 24.0$  Hz, 3 F), -155.81 (t,  $^3J_{\text{F-F}} = 21.4$  Hz, 3 F), -159.36 (t,  $^3J_{\text{F-F}} = 22.3$  Hz, 3 F), -163.22 (t,  $^3J_{\text{F-F}} = 21.4$  Hz, 3 F), -163.55 (t,  $^3J_{\text{F-F}} = 22.0$  Hz, 3 F), -164.20 (t,  $^3J_{\text{F-F}} = 22.6$  Hz, 3 F).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  114.20 (d,  $^1J_{\text{CH}} = 171.7$  Hz,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 113.62 (s,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 112.80 (s,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 111.29 (d,  $^1J_{\text{CH}} = 165.7$  Hz,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 106.57 (d,  $^1J_{\text{CH}} = 173.3$  Hz,  $\text{C}_5\text{H}_3\text{Me}_2$ ), 41.63 (q,  $^1J_{\text{C-H}} = 118.4$  Hz,  $\text{Zr-CH}_3$ ), 31.26 (q,  $^1J_{\text{CH}} = 116.5$  Hz,  $\text{B-CH}_3$ ), 22.21 (q,  $^1J_{\text{CH}} = 134.3$  Hz,  $\text{Zr-CH}_3\text{-Zr}$ ), 12.94 (q,  $^1J_{\text{CH}} = 128.0$  Hz,  $\text{C}_5\text{H}_2\text{Me}_2$ ), 12.71 (q,  $^1J_{\text{CH}} = 127.6$  Hz,  $\text{C}_5\text{H}_2\text{Me}_2$ ). Anal. Calcd for  $\text{C}_{68}\text{H}_{48}\text{BF}_{27}\text{Zr}_2$ : C, 51.98; H, 3.08; N, 0.00. Found: C, 51.61; H, 3.00; N, 0.00.

Analytical and spectroscopic data for  $\text{L} = \text{C}_5\text{Me}_5$  are as follows.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  1.57 (s, 60 H,  $\text{C}_5\text{Me}_5$ ), -0.84 (s, br, 3 H,  $\text{B-CH}_3$ ). The bridging and terminal methyl groups are discrete at low temperature.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ,  $-13^{\circ}\text{C}$ ):  $\delta$  -0.19 (s, br, 6 H,  $\text{Zr-CH}_3$ ), -0.92 (s, br, 3 H,  $\text{B-CH}_3$ ), -2.42 (s, br, 3 H,  $\text{Zr-CH}_3\text{-Zr}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^{\circ}\text{C}$ ):  $\delta$  -123.11 (d, s, br, 3 F), -139.27 (d,  $^3J_{\text{F-F}} = 20.3$  Hz, 3 F), -139.67 (t,  $^3J_{\text{F-F}}$

= 25.1 Hz, 6F), -155.73 (t,  $^3J_{F-F}$  = 20.9 Hz, 3 F), -160.91 (s, br, 3 F), -163.25 (t,  $^3J_{F-F}$  = 21.7 Hz, 3F), -163.56 (t,  $^3J_{F-F}$  = 22.0 Hz, 3 F), -164.13 (t,  $^3J_{F-F}$  = 21.4 Hz, 3 F). Anal. Calcd for  $C_{80}H_{72}BF_{27}Zr_2$ : C, 55.23; H, 4.17; N, 0.00. Found: C, 54.81; H, 3.98; N, 0.00.

#### 5 EXAMPLE 4

Synthesis of  $L_2Zr(H)(\mu-H)(H)ZrL_2^+ (MePBB)^-$   $L = C_5H_5, C_5H_3Me_2$

The procedure here is similar to that of Example 3, except that the reaction was carried out under 1 atm of  $H_2$  for 15 h: yields 81.6% ( $L = C_5H_5$ , grey solid) and 75.6% ( $L = C_5H_3Me_2$ , orange solid). Analytical and spectroscopic data for  $L = C_5H_5$  are as follows.  $^1H$  NMR ( $C_6D_6$ , 58°C):  $\delta$  6.67 (s, br, 2 H, Zr-H), 5.64 (s, 20 H,  $C_5H_5$ ), -0.81 (s, br, 3 H, B-CH<sub>3</sub>), -1.38 (s, br, 1 H, Zr-H-Zr). The chemical shifts and splitting patterns of  $^{19}F$  NMR are same as those of Example 3 ( $L = C_5H_5$ ). Anal. Calcd for  $C_{57}H_{26}BF_{27}Zr_2$ : C, 48.31; H, 1.85; N, 0.00. Found: C, 47.90; H, 1.92; N, 0.00.

Analytical and spectroscopic data for  $L = C_5H_3Me_2$  are as follows.  $^1H$  NMR ( $C_7D_8$ , 23°C):  $\delta$  5.81 (m, 4 H,  $C_5H_3Me_2$ ), 5.50 (m, 4 H,  $C_5H_3Me_2$ ), 5.23 (m, 4 H,  $C_5H_3Me_2$ ), 1.65 (m, 24 H,  $C_5H_3Me_2$ ), 0.25 (s, br, 2 H, Zr-H), -0.94 (s, br, 3 H, B-CH<sub>3</sub>), -1.52 (s, br, 1 H, Zr-H-Zr). The chemical shifts and splitting patterns of  $^{19}F$  NMR are same as those of Example 3 ( $L = C_5H_3Me_2$ ). Anal. Calcd for  $C_{65}H_{42}BF_{27}Zr_2$ : C, 51.05; H, 2.77; N, 0.00. Found: C, 51.07; H, -2.63; N, 0.00.

#### 20 EXAMPLE 5

Preparation of  $L_2ZrMe^+ (MePBB)^-$

5(a)  $L = C_5H_5$ . In a J-Young NMR tube, a small amount of a mixture of  $L_2ZrMe_2$  and PBB (1:1.2 molar ratio) was dissolved in  $C_6D_6$ . The NMR tube was then put in an NMR magnet and heated at 60°C. After 0.5 h,  $^1H$  NMR revealed the above monomeric species formed. The same structures were obtained by the reaction of the product of Example 3 with excess of PBB at 60°C for 0.5 h. In a real polymerization test, these species were also generated *in situ* by mixing  $L_2ZrMe_2$  and PBB at 60°C for 0.5 h.  $^1H$  NMR ( $C_6D_6$ , 60°C) for:  $\delta$  5.70 (s, 10 H,  $C_5H_5$ ), 0.14 (s, 3 H, Zr-CH<sub>3</sub>), -0.85 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}F$  NMR is similar to that of the corresponding dinuclear species of Example 3 ( $L = C_5H_5$ ).

5(b)  $L = C_5H_3Me_2$  The same procedure of Example 5 (a) was used to prepare this species. In the polymerization test, the following was observed:  $^1H$  NMR ( $C_7D_8$ ,  $60^\circ C$ ) for  $\delta$  5.68 (t,  $^3J_{H-H} = 2.8$  Hz, 4 H,  $C_5H_3Me_2$ ), 5.36 (t,  $^3J_{H-H} = 3.1$  Hz, 4 H,  $C_5H_3Me_2$ ), 5.23 (t,  $^3J_{H-H} = 2.8$  Hz, 4 H,  $C_5H_3Me_2$ ), 1.76 (s, 6 H,  $C_5H_3Me_2$ ), 1.56 (s, 6 H,  $C_5H_3Me_2$ ), 0.17 (s, 3 H, Zr-CH<sub>3</sub>), -0.93 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}F$  NMR of this species is similar to that of the corresponding dinuclear species of Example 3 ( $L = C_5Me_5$ ).  $^{13}C$  NMR ( $C_7D_8$ ,  $60^\circ C$ ):  $\delta$  117.74 ( $C_5H_3Me_2$ ), 112.14 ( $C_5H_3Me_2$ ), 108.01 ( $C_5H_3Me_2$ ), 42.11 (Zr-CH<sub>3</sub>), 34.43 (B-CH<sub>3</sub>), 12.63 ( $C_5H_2Me_2$ ), 12.45 ( $C_5H_2Me_2$ ).

5(c)  $L = C_5Me_5$  The same procedure of Example 5 (a) was used to prepare this species. In the polymerization test, the following was observed:  $^1H$  NMR ( $C_6D_6$ ,  $60^\circ C$ ):  $\delta$  1.61 (s, 30 H,  $C_5Me_5$ ), 0.13 (s, 3 H, Zr-CH<sub>3</sub>), -0.86 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}F$  NMR is similar to that of the corresponding dinuclear species of Example 3,  $L = C_5Me_5$ .

## EXAMPLE 6

### Synthesis of $LM(Me)_2^+ (MePBB)^- L = C_5Me_5$

$M = Ti$

The catalyst product of FIG. 5 was generated in the NMR tube reaction by mixing  $C_5Me_5TiMe_3$  and PBB at 1:1 molar ratio in  $C_6D_6$  for 2 h.  $^1H$  NMR ( $C_6D_6$ ,  $23^\circ C$ ):  $\delta$  9.03 (s, br, 2 H, CH<sub>2</sub>), 1.69 (s, 6 H,  $C_5Me_4$ ), 1.65 (s, 6 H,  $C_5Me_4$ ), 0.15 (s, 3 H, Ti-CH<sub>3</sub>), -0.82 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}F$  NMR is similar to that of Example 6.

## EXAMPLE 7

### Synthesis of $Me_2Si(tBuN-)(C_5Me_4)MMe^+ (MePBB)^-$

7(a)  $M = Zr$

$Me_2Si(tBuN-)(C_5Me_4)MMe_2$  (0.199 mmol) and PBB (0.199 mmol) were treated in the same manner as in the preparation of Example 1 except for the different reaction times (2 h). This procedure yields 73.1% (yellow solid). Analytical and spectroscopic data are as follows.  $^1H$  NMR ( $C_7D_8$ ,  $23^\circ C$ ):  $\delta$  1.73 (s, 3 H,  $C_5Me_4$ ), 1.69 (s, 3 H,  $C_5Me_4$ ), 1.63 (s, 3 H,  $C_5Me_4$ ), 1.43 (s, 3 H,  $C_5Me_4$ ), 0.85 (s, 9 H, N-*t*Bu), 0.28 (s, 3 H, SiMe<sub>2</sub>), 0.21 (s, 3 H, SiMe<sub>2</sub>), -0.48 (s, 3 H, Zr-CH<sub>3</sub>), -0.95 (s, br, 3 H, B-CH<sub>3</sub>).  $^{19}F$  NMR ( $C_7D_8$ ,  $23^\circ C$ ):  $\delta$  -124.20 (s, br, 3 F), -139.14 (d,  $^3J_{F-F} = 23.7$  Hz, 3 F), -139.35 (d,  $^3J_{F-F} = 22.0$  Hz, 3 F), -139.93 (d,  $^3J_{F-F} = 21.2$  Hz, 3 F), -155.79 (t,  $^3J_{F-F} = 21.2$  Hz, 3 F), -159.67 (t,  $^3J_{F-F} = 22.3$  Hz, 3 F), -163.28 (t,  $^3J_{F-F} = 21.7$  Hz, 3 F), -163.87 (t,  $^3J_{F-F} = 22.6$



Hz, 3 F), -164.13 (t,  $^3J_{F,F} = 22.6$  Hz, 3 F).  $^{13}\text{C}$  NMR ( $\text{C}_7\text{D}_8$ ,  $23^\circ\text{C}$ ):  $\delta$  114.05 ( $\text{C}_5\text{Me}_4$ ), 113.94 ( $\text{C}_5\text{Me}_4$ ), 112.58 ( $\text{C}_5\text{Me}_4$ ), 112.31 ( $\text{C}_5\text{Me}_4$ ), 112.02 ( $\text{C}_5\text{Me}_4$ ), 58.50 ( $\text{Zr-CH}_3$ ), 47.10 ( $\text{N-CMe}_3$ ), 34.37 ( $\text{N-CMe}_3$ ), 34.10 ( $\text{B-CH}_3$ ), 15.89 ( $\text{C}_5\text{Me}_4$ ), 13.46 ( $\text{C}_5\text{Me}_4$ ), 11.77 ( $\text{C}_5\text{Me}_4$ ), 10.99 ( $\text{C}_5\text{Me}_4$ ), 7.92 ( $\text{SiMe}_2$ ), 5.65 ( $\text{SiMe}_2$ ). Anal. Calcd for  $\text{C}_{53}\text{H}_{33}\text{BF}_{27}\text{NSiZr}$ : C, 47.97; H, 2.51; N, 1.06, Found: C, 47.79; H, 2.58; N, 0.86.

#### 7(b) M = Ti

The same procedure as Example 3 was followed:  $\text{Cp}'\text{TiMe}_3$  and PBB were mixed at a 1:1 molar ration in  $\text{C}_6\text{D}_6$  for 2 hours. 47.0% of an orange solid was recovered. Analytical and spectroscopic data are:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ):  $\delta$  9.03 (s, br, 2 H,  $\text{CH}_2$ ), 1.69 (s 6 H,  $\text{C}_5\text{Me}_4$ ), 1.65 (s 6 H,  $\text{C}_5\text{Me}_4$ ), 0.15 (s, 3 H,  $\text{Ti-CH}_3$ ), -0.82 (s, br, 3 H,  $\text{B-CH}_3$ ).  $^{19}\text{F}$  NMR is similar to that of 10.

**EXAMPLE 8****Ethylene Polymerization**

The reaction was conducted in a 250-mL flamed round bottom flask attached to a high vacuum line. The flask was equipped with a large magnetic stirring bar and a straight-bore high vacuum stopcock. The exterior connecting tube of the stopcock (Ca. 10mm in length) is sealed with a new serum cap. The reaction vessel is then evacuated down for several hours, back filled with inert gas (Ar), the stopcock closed and the reaction flask reevacuated. A measured amount of a nonpolar solvent such as benzene or toluene is vacuum transferred into the flask. Gaseous ethylene is admitted to the reaction flask through the purification column. The gas pressure is continuously maintained at 1 atm. Rapid stirring of the solution is initiated and after several minutes (to allow the saturation of the solvent with ethylene), the stopcock is opened and a small aliquot of catalyst solution (in the same solvent as used for the reaction) is injected by a gas-tight syringe just above the rapidly stirring solution through a serum cap (the syringe needle had been flattened so that the catalyst solution exits in a fine spray). Solid polyethylene is formed immediately. The reaction is quenched after a certain amount of time by injecting methanol through the serum cap on the stopcock. The solid polyethylene was collected by filtration, washed with methanol and then dried under vacuum at 100°C. Copolymerization may occur with the addition of a second monomer such as another  $\alpha$ -olefin.

Ethylene polymerizations were carried out at room temperature in 250-mL flamed, round-bottom flasks attached to a high-vacuum line. In a typical experiment, a solution of each of the catalysts of Example 3 in 2 mL of toluene was quickly injected using a gas-tight syringe equipped with a spraying needle into respective rapidly stirred flasks containing 100 mL of toluene which was pre-saturated under 1 atm of rigorously purified ethylene. In the case of the catalysts prepared in Example 4, the catalyst solution was generated *in situ* by mixing  $L_2ZrMe_2$  and PBB in 2 mL of toluene after aging for 0.5 h at 60°C, and then quickly injected into respective flasks under an ethylene atmosphere using a pre-warmed gas-tight syringe. The polymerization was quenched with acidic  $CH_3OH$  after a short time period (10-60 s) at which point voluminous quantities of polyethylene precipitated out. The respective polymeric products were collected by filtration, washed with methanol and dried under high vacuum to a constant weight.

**EXAMPLE 9****Ring-Opening Polymerization of THF**

A small amount of  $[(C_5H_3Me_2)_2ZrMe_2 \text{ } Zr \text{ } Me_2(C_5H_3Me_2)_2]^+ (MePBB)^-$  was loaded into a J-Young NMR tube and THF- $d_8$  was then vacuum-transferred into the tube. The mixture was slowly warmed to room temperature and left for several hours. The solid polymer formed in the tube was shown to be polytetrahydrofuran by  $^1H$  analysis.

**EXAMPLE 10****Propylene Polymerization**

This reaction is carried out in a 100mL quartz Worden vessel equipped with a magnetic stirring bar, a pressure gauge and a stainless steel o-ring assembly attached to a high vacuum line. In a typical experiment, the reaction vessel is flamed and then pumped under high vacuum for several hours, filled with inert gas and brought into a glove box. A measured amount of catalyst is added into the vessel. On the high vacuum line, a measured amount of the solvent and propylene are condensed at  $-78^\circ C$ . The reaction apparatus is sealed off and warmed to the desired temperature. During the polymerization process, the reaction tube is immersed in a large amount of tap water ( $20^\circ C$ - $25^\circ C$ ) or ice water ( $0^\circ C$ ) to help dissipate the heat produced from the polymerization and keep the temperature constant. The progress of the polymerization reactions is monitored through observance of the pressure change. After the reaction is finished (pressure drops to zero psi), the resulting oily liquid is removed from the vessel, washed with methanol and water and dried under vacuum at  $90$ - $100^\circ C$  for ten hours to result in a colorless oil.

Table II sets forth the relevant data concerning propylene polymerization utilizing the catalyst prepared according to the enumerated example.

**TABLE II**

| Example:                  | 9                             | 10                       |
|---------------------------|-------------------------------|--------------------------|
| Metallocene Cation/Anion* | $(Cp_2)ZrMe)_2Me^+/(MePBB)^-$ | $(Cp_2ZrMe^+)/(MePBB)^-$ |
| catalyst (mM)             | 0.15                          | 0.15                     |
| Reaction time(m)          | 40                            | 40                       |
| Yield (g)                 | 4.0                           | 5.0                      |
| *Cp = $C_5H_5$            |                               |                          |

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments and equivalents falling within the scope of the appended claims.

Various features of the invention are set forth in the following claims.

What is claimed is:

1. A catalytic complex of the structure:  $(LL' MR)^+ (RBR'R''_2)^-$  where
 

|         |   |   |
|---------|---|---|
| L, L'   | = | $C_5H_nR_{5-n}$ , indenyl, allyl, benzyl, $C_5H_nR_{4-n}XNR$                          |
| M       | = | early transition metal or actinide  |
| X       | = | $R_2'''Si, R'''$ bridging alkyl or aryl group ( $C \leq 10$ )                         |
| R, R''' | = | alkyl, benzyl, or aryl group ( $C \leq 20$ ), hydride, silyl;                         |
| B       | = | Boron   |
| R'      | = | fluorinated biphenyl  |
| R''     | = | fluorinated phenyl, fluorinated biphenyl, or fluorinated polycyclic fused ring groups |
2. The complex of Claim 1 wherein  $M = Ti, Zr, Hf, Th, \text{ or } U$ .
3. The complex of Claim 1 wherein said polycyclic fused ring groups include naphthyl, anthryl, and fluorenyl.
4. A method of preparing a catalyst including the steps of adding a compound of the formula  $LL' MRR'$ , where
 

|         |   |   |
|---------|---|---|
| L, L'   | = | $C_5H_nR_{5-n}$ , indenyl, allyl, benzyl, $C_5H_nR_{4-n}XNR$  |
| M       | = | early transition metal or actinide  |
| X       | = | $R_2'''Si, R'''$ bridging alkyl or aryl group ( $C \leq 10$ )   |
| R, R''' | = | alkyl, benzyl, or aryl group ( $C \leq 20$ ), hydride, silyl<br>to perfluorobiphenylborane in a nonpolar solvent. |
5. The method of Claim 4 wherein M is selected from the group consisting of Ti, Zr, Hf, Th and U.
6. The method of claim 4 wherein said polycyclic fused ring groups include naphthyl, anthryl, and fluorenyl.
7. The method of Claim 4 wherein the solvent is selected from the group consisting of benzene, toluene, pentane or other non-polar solvents.

8. The method of Claim 4 wherein said catalyst is prepared at  $-78^{\circ}\text{C}$ .

9. The method of Claim 4 wherein said catalyst is prepared at room temperature.

10. A method of polymerizing a monomer or copolymerizing a mixture of monomers comprising the steps of adding a catalyst  $(\text{LL}'\text{MR})^+(\text{RBR}'\text{R}'')$  to said monomer where

- |    |         |   |   |
|----|---------|---|---|
|    | L, L'   | = | $\text{C}_5\text{H}_n\text{R}_{5-n}$ , indenyl, allyl, benzyl, $\text{C}_5\text{H}_n\text{R}_{4-n}\text{XNR}$ |
| 5  | M       | = | early transition metal or actinide  |
|    | X       | = | $\text{R}_2'''\text{Si}, \text{R}'''$ bridging alkyl or aryl group ( $\text{C} \leq 10$ )                     |
|    | R, R''' | = | alkyl, benzyl, or aryl group ( $\text{C} \leq 20$ ), hydride, silyl;  |
|    | B       | = | Boron   |
|    | R'      | = | fluorinated biphenyl  |
| 10 | R''     | = | fluorinated phenyl, fluorinated biphenyl, or fluorinated polycyclic fused rings                               |

11. The method of Claim 10 wherein said reaction is carried out at ambient conditions.

12. The method of Claim 10 wherein said reaction is initiated at  $-78^{\circ}\text{C}$  and slowly warmed to ambient temperatures.

13. The method of Claim 10 wherein said reaction is carried out at a temperature from  $-78^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ .

14. The method of Claim 10 wherein said monomer is ethylene.

15. The method of Claim 10 wherein said monomer is propylene.

16. The method of Claim 10 wherein said polymerizing comprises primarily an oligomerization reaction.

17. The method of Claim 10 wherein said polymerization comprises primarily a dimerization reaction.
18. The method of Claim 10 wherein said monomer is added to a second monomer to result in a copolymerization reaction.
19. The method of Claim 10 wherein said monomer is Tetrahydrofuran.

FIG. 1

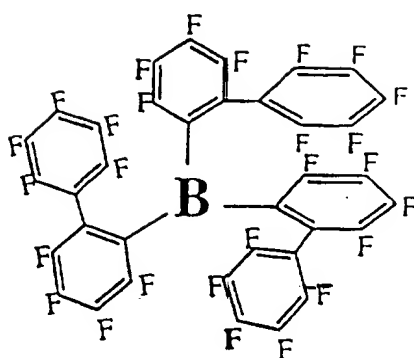




FIG. 2

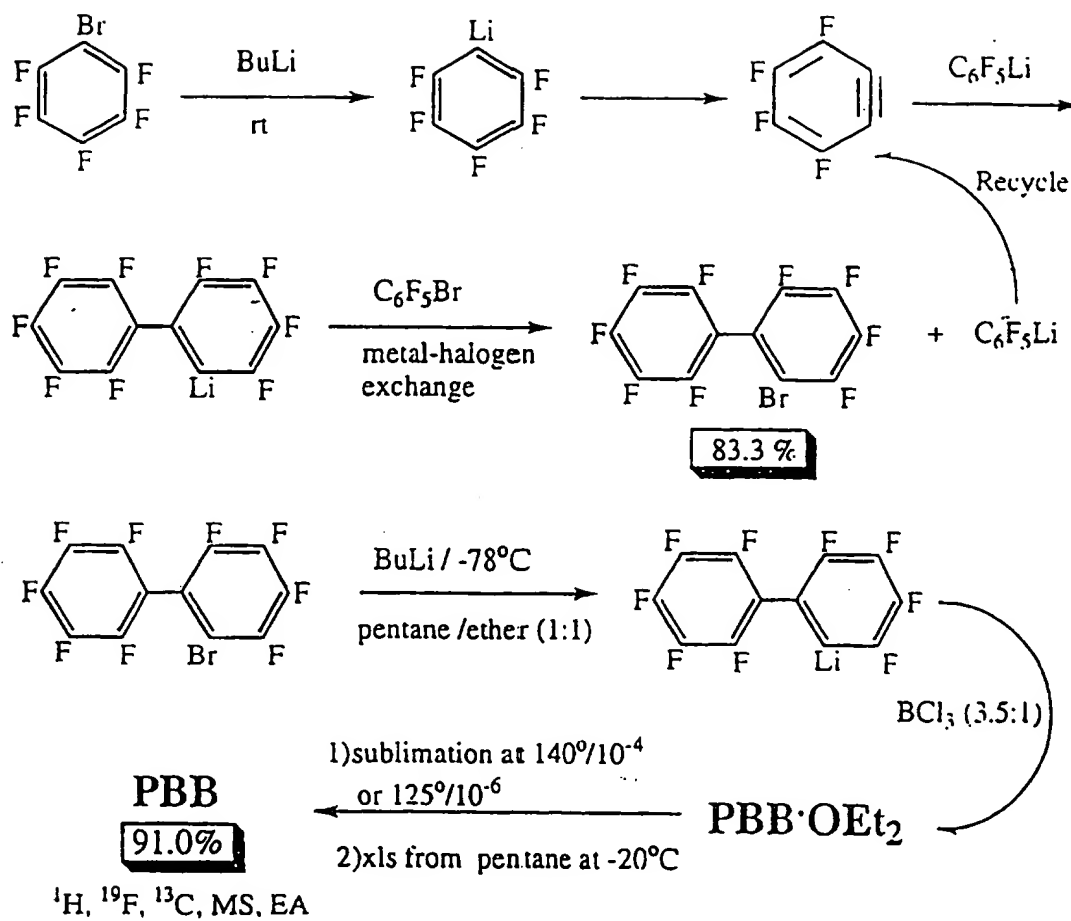


FIG. 3

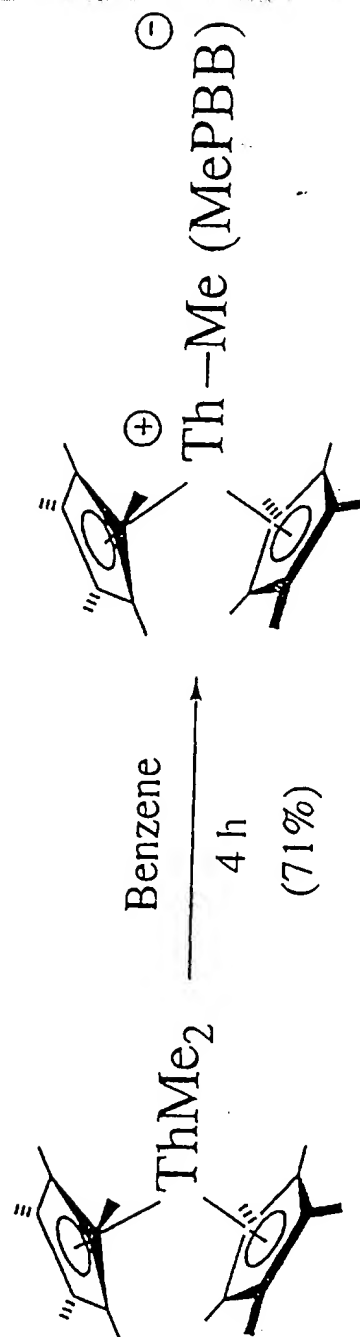


FIG. 4

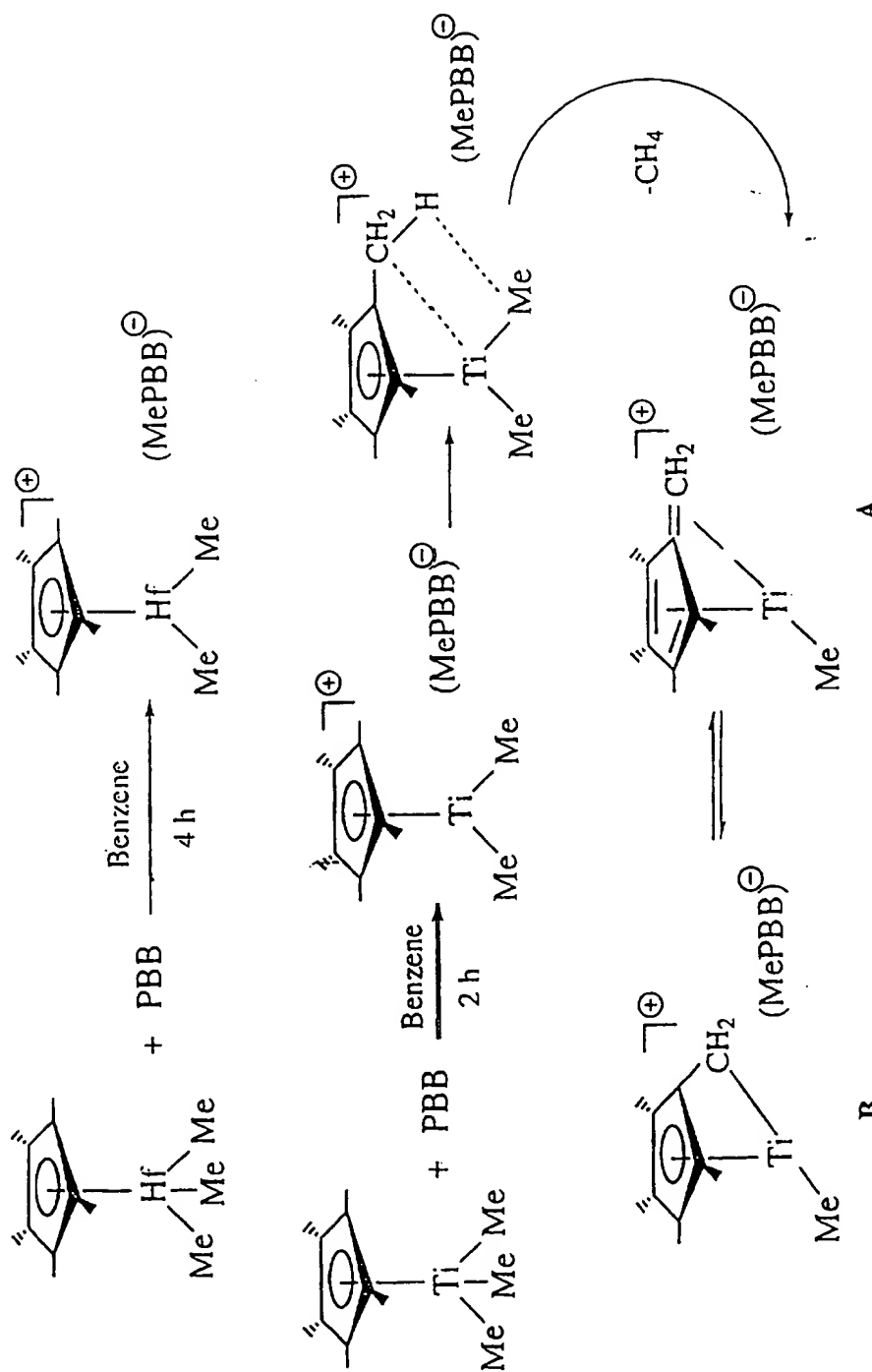


FIG. 5

FIG. 6

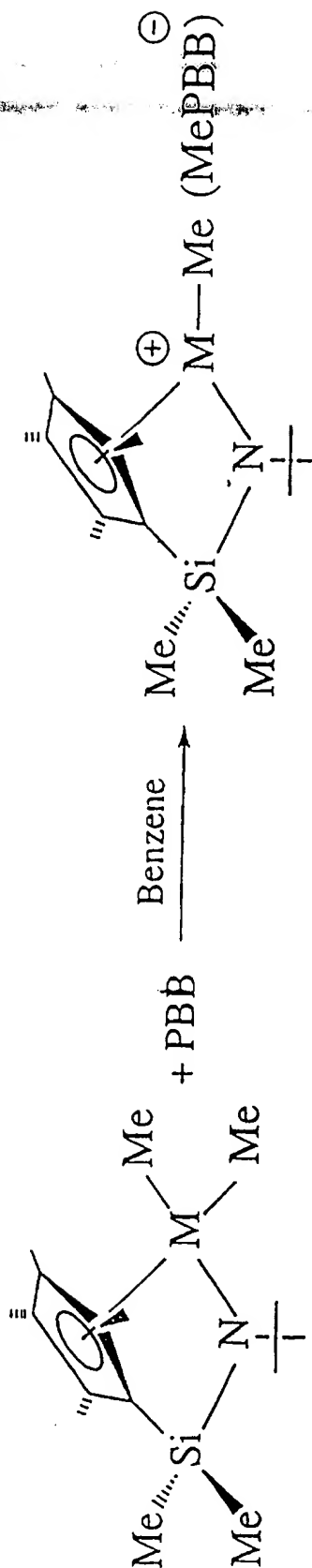
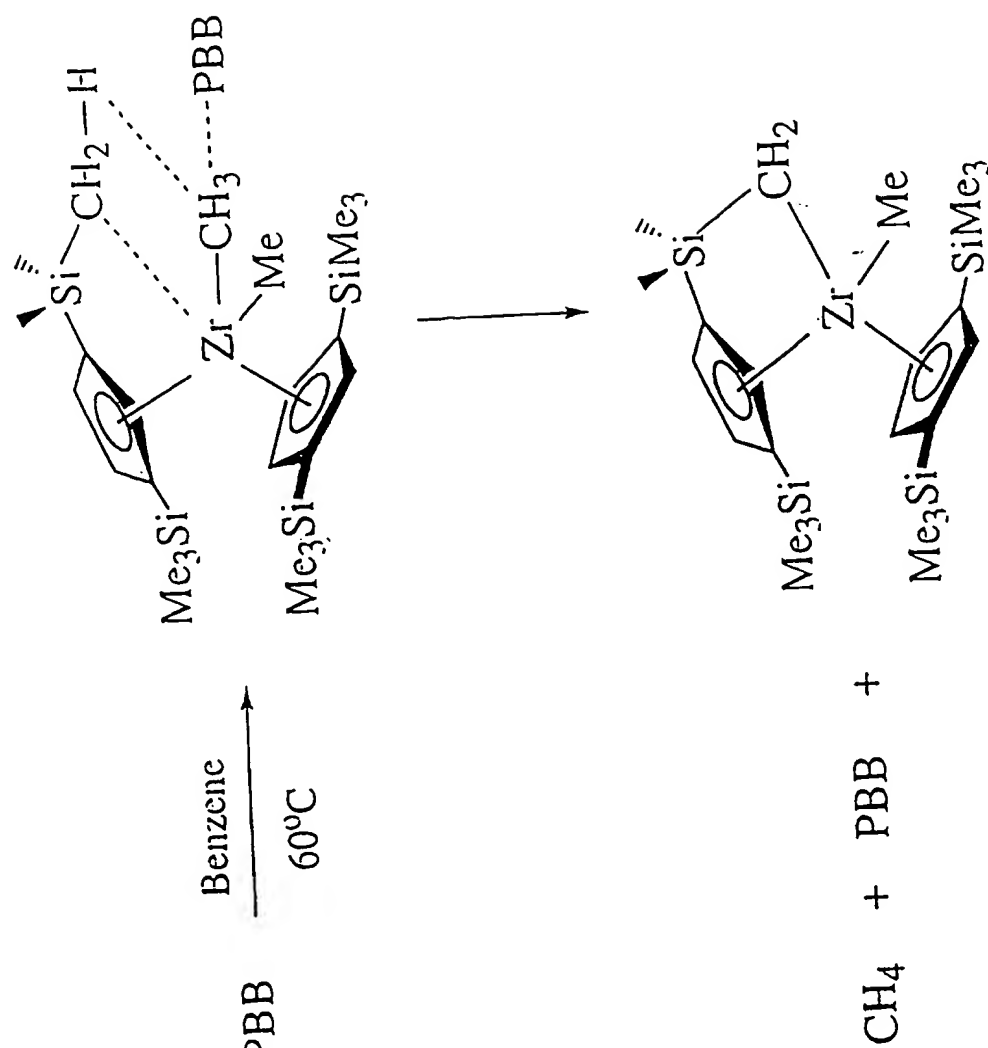


FIG. 7



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/02548**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : B01J 31/00, 37/00; C07E 5/00, 7/00, 17/00

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 534/11; 556/7, 11, 12, 53; 502/104, 117, 152, 158; 526/126, 127, 133, 134, 160, 170, 351, 352

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
REGISTRY and CA Databases**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                    | Relevant to claim No. |
|-----------|---|-----------------------|
| Y,E       | US 5,486,632 A (DEVORE et al.) 23 January 1996, column 27, lines 53-63 through column 28, lines 1-54. | 4-18                  |
| Y         | EP 0 468 651 A1 (THE DOW CHEMICAL COMPANY) 29 January 1992, see Examples and claims.                  | 4-18                  |
| A         | EP 0 561 479 A1 (EXXON CHEMICAL PATENTS, INC.) 22 September 1993, see entire document.                | 1-19                  |
| A         | US 5,064,802 A (STEVENS et al.) 12 November 1991, see entire document.                                | 1-19                  |

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

|   |  |
|---|--|
| * Special categories of cited documents:  | *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
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| *E* earlier document published on or after the international filing date  | *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *G* document member of the same patent family  |
| *O* document referring to an oral disclosure, use, exhibition or other means  |  |
| *P* document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

02 JUNE 1997

Date of mailing of the international search report

25 JUN 1997

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/02548

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

534/11; 556/7, 11, 12, 53; 502/104, 117, 152, 158; 526/126, 127, 133, 134, 160, 170, 351, 352

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